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Key indicators

Ammonium iron(III) molybdate

A new compound with an open framework, $(NH_4)[Fe(MoO_4)_2]$, was synthesized through hydrothermal reaction. It contains 10 non-H atoms in the asymmetric unit and the structure comprises a network of FeO_6 octahedra and MoO_4 tetrahedra that strictly alternate and involve only Fe—O—Mo linkages. The ammonium cations sit in the middle of the channels formed by these linkages.

Comment

The field of open-framework inorganic materials has expanded dramatically during the last decade. These materials, which find utility in catalysis, separations and ion-exchange, include a large number of main-group phosphates, such as those of aluminium, gallium and indium, as well as several transition metal phosphates (Muller & Kogerler, 1999). Replacement of phosphate by molybdate in the framework led to new series of open-framework inorganic materials, which, to our knowledge, have rarely been reported (Reiff *et al.*, 1997; Ehrenberg *et al.*, 1999). Reported here are the synthesis and X-ray crystal structure of a new compound, $(NH_4)[Fe(MoO_4)_2]$ (I), with an open framework which is built up from FeO_6 octahedra and MoO_4 tetrahedra.

(I)
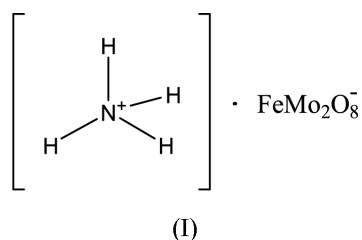
There are two crystallographically independent Mo atoms and one Fe atom in the title compound. The O atoms of the molybdate groups are linked to three adjacent iron atoms, with the fourth coordination site corresponding to a terminal Mo—O group, as evidenced by the short Mo—O distances [1.715 (3) and 1.702 (3) Å, respectively]. The iron atom is octahedrally coordinated by six O atoms from six MoO_4 tetrahedra. By means of the Fe—O—Mo linkages, the polyhedral connectivity in the title compound leads to an open-framework network. One of the axial and two equatorial coordination sites on the iron are shared with three different molybdate groups, to constitute a two-dimensional corrugated sheet in the *bc* plane, as shown in Fig. 1. The other three sites on the iron atom are bound to three other different molybdate groups, which interact with the layers above and below, thus leading to an extended framework. This mode of connectivity
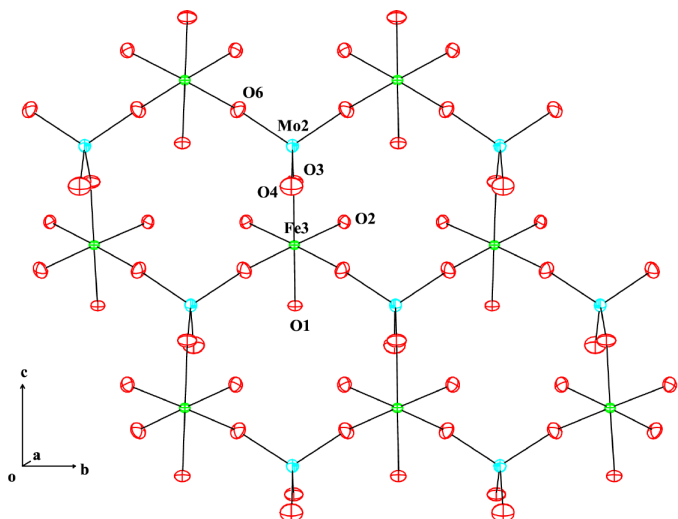
Figure 1
The two-dimensional corrugated sheet in the title compound. Displacement ellipsoids are drawn at the 50% probability level.
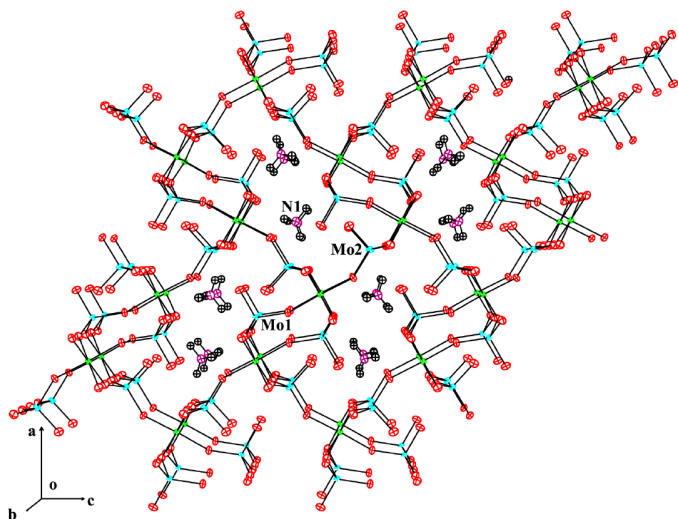
Figure 2
Three-dimensional framework of the title compound; the ammonium cation sits in the middle of the channels along the *b* axis. Displacement ellipsoids are drawn at the 50% probability level.

generates the 12-membered one-dimensional channel, of width 4.5×11.1 Å (O atom-to-O atom) along the *b* axis, as shown in Fig. 2.

Extensive bond-valence-sum calculations (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) indicated the valences of Fe, Mo and O to be +3, +6 and −2, respectively, and the framework stoichiometry works out to be $Fe(MoO_4)_2$. This results in the framework composition consisting of an Mo/Fe ratio of 2.0 and having a charge of −1. Charge compensation is achieved by an extra-framework ammonium cation. Thus, the ammonium cations are located in the channels.

Experimental

FeCl$_3$·6H$_2$O (0.27 g, 1.0 mmol) and (NH$_4$)$_6$Mo$_7$O$_{24}$·6H$_2$O (1.24 g, 1.0 mmol) were mixed in 4.0 ml distilled water, and the resulting pH

was adjusted to 6.5 by 1.0 *M* NaOH solution. The mixture was stirred for few minutes, sealed in a stainless steel (25 ml) Teflon-lined vessel and heated at 443 K under autogenous pressure for 60 h. After cooling to room temperature, the brown block-shaped crystals were filtered off, washed with distilled water and dried in air.

Crystal data

(NH$_4$)[Fe(MoO$_4$)$_2$]	Mo $K\alpha$ radiation
$M_r = 393.77$	Cell parameters from 25
Orthorhombic, $Pnma$	reflections
$a = 14.782$ (3) Å	$\theta = 12–18°$
$b = 5.6774$ (11) Å	$\mu = 5.31$ mm^{-1}
$c = 8.7653$ (18) Å	$T = 293$ (2) K
$V = 735.6$ (3) Å^3	Block, brown
$Z = 4$	$0.15 \times 0.14 \times 0.14$ mm
$D_x = 3.556$ Mg m^{-3}	

Data collection

Rigaku Weissenberg IP diffractometer	870 reflections with $I > 2\sigma(I)$
φ scans	$\theta_{max} = 27.5°$
Absorption correction: none	$h = 0 \to 19$
932 measured reflections	$k = 0 \to 7$
932 independent reflections	$l = 0 \to 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$+ 0.1878P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
932 reflections	$\Delta\rho_{max} = 1.35$ e Å^{-3}
71 parameters	$\Delta\rho_{min} = -1.20$ e Å^{-3}
H-atom parameters not refined	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
	Extinction coefficient: 0.0084 (5)

Table 1
Selected geometric parameters (Å).

Mo1—O5	1.715 (3)	Mo2—O4	1.795 (2)
Mo1—O1	1.758 (3)	Fe3—O4	1.981 (3)
Mo1—O2	1.7959 (17)	Fe3—O1	1.994 (3)
Mo2—O3	1.702 (3)	Fe3—O6^i	1.9972 (18)
Mo2—O6	1.784 (2)	Fe3—O2^{ii}	2.0178 (17)

Symmetry codes: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $-x, -y, 1 - z$.

The positions of atoms H1 and H2 were found in a difference Fourier map on the basis of the N—H distance and the H—N—H angle; their positions were then fixed. Atom H3 was refined using a riding model. Failure of the diffractometer made it impossible to check the standard reflections or to make an absorption correction. However, given the shape of the crystal and the good agreement factors, we believe that making an absorption correction would not significantly change the results we report. The highest peak is located 0.83 Å from O1 and the deepest hole 0.01 Å from Mo1.

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

inorganic papers

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Ehrenberg, H., Svoboda, I., Wiesmann, M. & Weitzel, H. (1999). *Acta Cryst.* C**55**, 1383–1384.

McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.

Molecular Structure Corporation (1999). *TEXSAN* (Version 1.10) and *TEXRAY*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Muller, A. & Kogerler, P. (1999). *Coord. Chem. Rev.* **182**, 3–17.

Reiff, W. M., Zhang, J. H., Tam, H. & Attfield, J. P. (1997). *J. Solid State Chem.* **130**, 147–151;

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.